

## CLAIMS

**What is claimed is:**

1. A process for reducing the amount of residual aromatic diisocyanate monomer in a polyurethane prepolymer reaction product comprising distilling the product in the presence of at least one inert solvent having a boiling point about 1°C to about 100°C below the boiling point of the diisocyanate monomer at a pressure of 10 torr, wherein the aromatic diisocyanate monomer has a boiling point above about 200°C at 10 torr, the weight ratio of the inert solvent to the residual aromatic diisocyanate monomer ranges from about 90:10 to about 10:90, and the inert solvent comprises about 5% to about 85% by weight of the total weight of the combination of the prepolymer reaction product mixture plus solvents.
2. The process of claim 1 wherein the monomeric diisocyanate is at least one isomer of diphenylmethane diisocyanate.
3. The process of claim 2 wherein the inert solvent is selected from the group consisting of organic aromatic, aliphatic esters, and mixtures thereof having boiling points in the range of from about 115°C to about 214°C at 10 torr.
4. The process of claim 2 wherein the distillation step comprises at least three agitated film vacuum distillation stages in series, each at an evaporative temperature of up to about 150°C.

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- 1       5. A prepolymer comprising the reaction product of a polyol and a stoichiometric  
2 excess of diphenylmethane diisocyanate monomer at an NCO:OH ratio in the range  
3 of from about 2:1 to about 20:1, wherein the unreacted diisocyanate monomer is  
4 removed by a process comprising distilling the reaction product in the presence of at  
5 least one inert solvent having a boiling point about 1°C to about 100°C below the  
6 boiling point of the diphenylmethane diisocyanate monomer at a pressure of 10 torr,  
7 wherein the weight ratio of the inert solvent to the residual diphenylmethane  
8 diisocyanate monomer ranges from about 90:10 to about 10:90, and the inert solvent  
9 comprises about 5% to about 85% by weight of the total weight of the combination of  
10 the prepolymer reaction product mixture plus solvents.
- 1       6. The prepolymer of claim 5 containing less than 0.3% by weight of unreacted  
2 diphenylmethane diisocyanate monomer.
- 1       7. The prepolymer of claim 6 containing less than 0.1% by weight of unreacted  
2 diphenylmethane diisocyanate monomer.
- 1       8. The prepolymer of claim 6 containing less than 0.05% by weight of unreacted  
2 diphenylmethane diisocyanate monomer and containing at least about 80% of the  
3 theoretical NCO content for a pure ABA structure.
- 1       9. The prepolymer of claim 6 wherein the polyol is selected from the group  
2 consisting of a polyester of adipic acid; a polyether of ethylene oxide, propylene

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3      oxide, or tetrahydrofuran; a polycaprolactone; a polycarbonate; a hydrocarbon polyol;  
4      and mixtures thereof; said polyol having a molecular weight in the range of from  
5      about 400 to about 5000.

1      10.     The prepolymer of claim 5 wherein the polyol comprises at least one  
2      component having a low molecular weight in the range of from about 62 to about  
3      400, and selected from the group consisting of ethylene glycol, isomers of propylene  
4      glycol, isomers of butane diol, hexanediol, trimethylolpropane, pentaerythritol,  
5      poly(tetramethylene ether) glycol, diethylene glycol, triethylene glycol, dipropylene  
6      glycol, tripropylene glycol, and mixtures thereof.

1      11.     The prepolymer of claim 10 further comprising at least one polyol having a  
2      high molecular weight in the range of from about 400 to about 5000.

1      12.     The prepolymer of claim 11 wherein the molar ratio of the low molecular  
2      weight polyol to the high molecular polyol is in the range of from about 0.25 to about  
3      2.5:1.

1      13.     A polyurethane prepolymer terminated with diphenylmethane diisocyanate,  
2      said prepolymer comprising no more than about 0.3% free diphenylmethane  
3      diisocyanate and having at least about 80% of the theoretical NCO content for pure  
4      ABA structure.

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1       14. A polyurethane elastomer comprising the reaction product of i) a prepolymer  
2 terminated with diphenylmethane diisocyanate, said prepolymer comprising no more  
3 than about 0.3% free diphenylmethane diisocyanate and having at least about 80% of  
4 theoretical NCO content for pure ABA structure with ii) a chain extender selected  
5 from the group consisting of 1,4-butanediol; 1,3-propanediol; ethylene glycol;  
6 1,6-hexanediol; hydroquinone-bis-hydroxyethyl ether; resorcinol di(beta-hydroxyethyl)  
7 ether; resorcinol di(beta-hydroxypropyl) ether; 1,4-cyclohexane dimethanol; an  
8 aliphatic triol; an aliphatic tetrol; 4,4'-methylene-bis(2-chloroaniline); 4,4'-methylene-  
9 bis(3-chloro-2,6-diethylaniline); diethyl toluene diamine; t-butyl toluene diamine;  
10 dimethylthio-toluene diamine; trimethylene glycol di-p-amino-benzoate;  
11 methylenedianiline; methylenedianiline-sodium chloride complex; and mixtures  
12 thereof;  
13 wherein the equivalent ratio of prepolymer to chain extender is in the range of from  
14 about 0.7:1 to about 1.2:1.

1       15. The elastomer of claim 14 wherein at least one chain extender is selected from  
2 the group consisting of trimethylene glycol di-p-amino-benzoate; 4,4'-methylene-  
3 bis(3-chloroaniline); 4,4'-methylene-bis(3-chloro-2,6-diethylaniline); diethyl toluene  
4 diamine; and dimethylthio-toluene diamine.

1       16. The elastomer of claim 14 wherein the chain extender is trimethylene glycol  
2 di-p-amino-benzoate.

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1      17. The elastomer of claim 14 wherein the chain extender is 4,4'-methylene-bis(2-  
2      chloroaniline).

1      18. The elastomer of claim 14 wherein the chain extender is diethyl toluene  
2      diamine.

1      19. A polyurethane elastomer comprising the reaction product of:

2            A) a diphenylmethane diisocyanate-terminated prepolymer comprising the  
3      reaction product of:

4                i) a first polyol comprising at least one component having a low  
5      molecular weight in the range of from about 62 to about 400, and selected from the  
6      group consisting of ethylene glycol, isomers of propylene glycol, isomers of butane  
7      diol, hexanediol, trimethylolpropane, pentaerythritol, poly(tetramethylene ether)  
8      glycol, diethylene glycol, triethylene glycol, dipropylene glycol, tripropylene glycol, and  
9      mixtures thereof;

10               ii) a second polyol having a high molecular weight in the range of  
11      from about 400 to about 5000; and

12               iii) a stoichiometric excess of diphenylmethane diisocyanate  
13      monomer at an NCO:OH ratio in the range of from about 2:1 to about 20:1;  
14      wherein unreacted diphenylmethane diisocyanate monomer is removed from said  
15      reaction product by a process comprising distilling the reaction product in the  
16      presence of at least one inert solvent having a boiling point about 1°C to about 100°C  
17      below the boiling point of the diphenylmethane diisocyanate monomer at a pressure

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18 of 10 torr, wherein the weight ratio of the inert solvent to the residual  
19 diphenylmethane diisocyanate monomer ranges from about 90:10 to about 10:90, and  
20 the inert solvent comprises about 5% to about 85% by weight of the total weight of  
21 the combination of the prepolymer reaction product mixture plus solvents; with  
22       B) a chain extender selected from the group consisting of 1,4-butanediol;  
23 1,3-propanediol; ethylene glycol; 1,6-hexanediol; hydroquinone-bis-hydroxyethyl ether;  
24 resorcinol di(beta-hydroxyethyl) ether; resorcinol di(beta-hydroxypropyl) ether;  
25 1,4-cyclohexane dimethanol; aliphatic triols; aliphatic tetrols; 4,4'-methylene-bis(2-  
26 chloroaniline); 4,4'-methylene-bis(3-chloro-2,6-diethylaniline); diethyl toluene  
27 diamine; t-butyl toluene diamine; dimethylthio-toluene diamine; trimethylene glycol  
28 di-p-amino-benzoate; methylenedianiline; methylenedianiline-sodium chloride  
29 complex; and mixtures thereof;  
30 wherein the equivalent ratio of chain extender to prepolymer is in the range of from  
31 about 0.7:1 to about 1.2:1.

1 20. A wheel or roll comprising a core and a polyurethane cover wherein the cover  
2 comprises the reaction product of :  
3       A) a prepolymer comprising the reaction product of a polyol and diphenyl  
4 methane diisocyanate wherein excess diphenyl methane diisocyanate has been  
5 removed to less than 2 wt% , and  
6       B) an amine or diol chain extender.

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1       21. The wheel or roll of claim 20 wherein the amine or diol chain extender is  
2 selected from the group consisting of 1,4-butanediol; 1,3-propanediol; ethylene glycol;  
3 1,6-hexanediol; hydroquinone-bis-hydroxyethyl ether; resorcinol di(beta-hydroxyethyl)  
4 ether; resorcinol di(beta-hydroxypropyl) ether; 1,4-cyclohexane dimethanol; an  
5 aliphatic triol; an aliphatic tetrol; 4,4'-methylene-bis(2-chloroaniline); 4,4'-methylene-  
6 bis(3-chloro-2,6-diethylaniline); diethyl toluene diamine; t-butyl toluene diamine;  
7 dimethylthio-toluene diamine; trimethylene glycol di-p-amino-benzoate;  
8 methylenedianiline; methylenedianiline-sodium chloride complex; and mixtures  
9 thereof.

1       22. A wheel or roll comprising a core and a polyurethane cover wherein the cover  
2 comprises a polyurethane elastomer comprising the reaction product of i) a  
3 prepolymer terminated with diphenylmethane diisocyanate, said prepolymer  
4 comprising no more than about 0.3% free diphenylmethane diisocyanate and having  
5 at least about 80% of theoretical NCO content for pure ABA structure with ii) a  
6 chain extender selected from the group consisting of 1,4-butanediol; 1,3-propanediol;  
7 ethylene glycol; 1,6-hexanediol; hydroquinone-bis-hydroxyethyl ether; resorcinol  
8 di(beta-hydroxyethyl) ether; resorcinol di(beta-hydroxypropyl) ether; 1,4-cyclohexane  
9 dimethanol; an aliphatic triol; an aliphatic tetrol; 4,4'-methylene-bis(2-chloroaniline);  
10 4,4'-methylene-bis(3-chloro-2,6-diethylaniline); diethyl toluene diamine; t-butyl  
11 toluene diamine; dimethylthio-toluene diamine; trimethylene glycol di-p-amino-  
12 benzoate; methylenedianiline; methylenedianiline-sodium chloride complex; and  
13 mixtures thereof;

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14 wherein the equivalent ratio of prepolymer to chain extender is in the range of from  
15 about 0.7:1 to about 1.2:1.

1 23. A golf ball comprising a core and a cover, where the cover is a polyurethane  
2 elastomer comprising the reaction product of:

3 A) a prepolymer comprising the reaction product of a polyol and diphenyl  
4 methane diisocyanate wherein excess diphenyl methane diisocyanate has been  
5 removed to less than 2 wt%, and

6 B) at least one hydroxy or amine functional chain extender.

10 24. The golf ball of claim 23 wherein the amine or diol chain extender is selected  
11 from the group consisting of 1,4-butanediol; 1,3-propanediol; ethylene glycol;  
12 1,6-hexanediol; hydroquinone-bis-hydroxyethyl ether; resorcinol di(beta-hydroxyethyl)  
13 ether; resorcinol di(beta-hydroxypropyl) ether; 1,4-cyclohexane dimethanol; an  
14 aliphatic triol; an aliphatic tetrol; 4,4'-methylene-bis(2-chloroaniline); 4,4'-methylene-  
15 bis(3-chloro-2,6-diethylaniline); diethyl toluene diamine; t-butyl toluene diamine;  
16 dimethylthio-toluene diamine; trimethylene glycol di-p-amino-benzoate;  
17 methylenedianiline; methylenedianiline-sodium chloride complex; and mixtures  
18 thereof

1 25. A golf ball comprising a core and a polyurethane cover wherein the cover  
2 comprises a polyurethane elastomer comprising the reaction product of i) a  
3 prepolymer terminated with diphenylmethane diisocyanate, said prepolymer

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4 comprising no more than about 0.3% free diphenylmethane diisocyanate and having  
5 at least about 80% of theoretical NCO content for pure ABA structure with ii) a  
6 chain extender selected from the group consisting of 1,4-butanediol; 1,3-propanediol;  
7 ethylene glycol; 1,6-hexanediol; hydroquinone-bis-hydroxyethyl ether; resorcinol  
8 di(beta-hydroxyethyl) ether; resorcinol di(beta-hydroxypropyl) ether; 1,4-cyclohexane  
9 dimethanol; an aliphatic triol; an aliphatic tetrol; 4,4'-methylene-bis(2-chloroaniline);  
10 4,4'-methylene-bis(3-chloro-2,6-diethylaniline); diethyl toluene diamine; t-butyl  
11 toluene diamine; dimethylthio-toluene diamine; trimethylene glycol di-p-amino-  
12 benzoate; methylenedianiline; methylenedianiline-sodium chloride complex; and  
13 mixtures thereof;  
14 wherein the equivalent ratio of prepolymer to chain extender is in the range of from  
15 about 0.7:1 to about 1.2:1.

14 26. A multicomponent system for producing polyurea-urethane elastomers

2 comprising

- 3       A)     a prepolymer comprising the reaction product of a polyol and diphenyl  
4     methane diisocyanate wherein excess diphenyl methane diisocyanate has been  
5     removed to less than 2 wt%, and  
6       B)     methylene dianiline or its complex with sodium chloride.

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- 1        27. A reversibly blocked prepolymer comprising the reaction product of  
2            A) a prepolymer comprising the reaction product of a polyol and diphenyl  
3            methane diisocyanate wherein excess diphenyl methane diisocyanate has been  
4            removed to less than 2 wt%, and  
5            B) at least one blocking agent consisting of a ketoxime, a phenol, a lactam,  
6            or a pyrazole.
- 1        28. A thermoplastic urethane elastomer comprising the reaction product of  
2            A) a prepolymer comprising the reaction product of a polyol and diphenyl  
3            methane diisocyanate wherein excess diphenyl methane diisocyanate has been  
4            removed to less than 2 wt%, and  
5            B) at least one hydroxy or amine functional chain extender.